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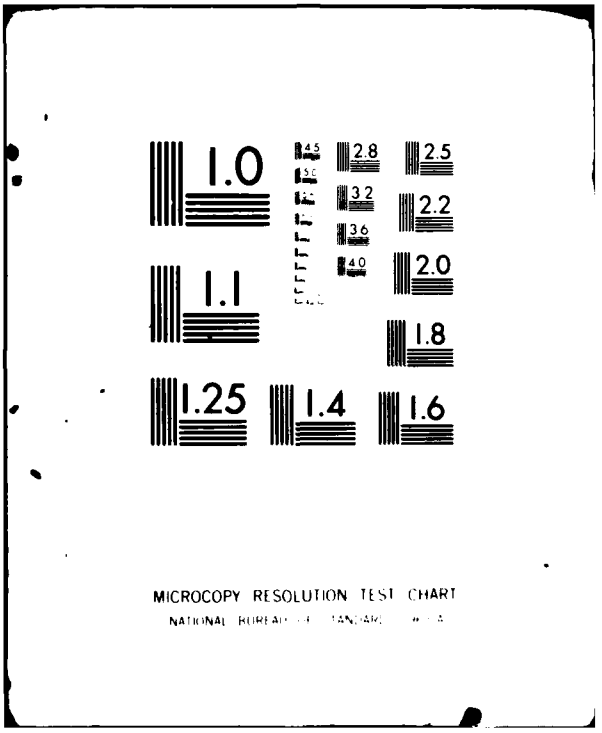
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SPECTRAL DIFFUSION IN ORIENTATIONALLY DISORDERED ORGANIC SOLIDS

by

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The spectral diffusion within the inhomogeneous linewidth of the $T_1 \leftarrow S_0$ transition is presented for an orientationally disordered organic solid under the condition when kT (~ 3 cm^{-1}) is much smaller than the inhomogeneous linewidth (~ 83 cm^{-1}). The rate of the transfer is found to increase as the site energy increases. This result is explained in terms of a phonon assisted unidirectional (high to low) energy transfer process in which the increasing density of the low energy sites (acceptors) with an increase in the excitation energy plays an important role.

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SPECTRAL DIFFUSION IN ORIENTATIONALLY DISORDERED ORGANIC SOLIDS

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ABSTRACT

The spectral diffusion within the inhomogeneous linewidth of the $T_1 \leftarrow S_0$ transition is presented for an orientationally disordered organic solid under the condition when kT ($\sim 3\ cm^{-1}$) is much smaller than the inhomogeneous linewidth ($\sim 83\ cm^{-1}$). The rate of the transfer is found to increase as the site energy increases. This result is explained in terms of a phonon assisted unidirectional (high to low) energy transfer process in which the increasing density of the low energy sites (acceptors) with an increase in the excitation energy plays an important role.

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INTRODUCTION

Great interest has recently developed in the optical properties of, and energy transfer in, amorphous solids, e.g., inorganic glasses. Both the inhomogeneous and homogeneous linewidths for T less than ~ 100K of electronic transitions of impurity ions in these solids are found to be broader than in crystalline solids[1,2]. Fluorescence line narrowing techniques[3] have recently been used to study the spectral diffusion of the $^5D_o \leftarrow {}^7F_o$ transition energy of Eu^{3+} amongst different sites in calcium metaphosphate glass at temperatures (200^o - 350^o K) where kT is greater than the inhomogeneous width (~ 50 cm^{-1}). The results suggest[4] that the transfer is dipolar in nature, phonon assisted, and is independent of the donor site-engergy within the inhomogeneous profile. Indications are that the diffusion limit (i.e., the limit when the spectral diffusion coefficient is independent of time) is reached only when the excitation level of the donor is reduced to 5% of its initial value at room temperature and 30 mole percent Eu^{3+} concentration[5].

Orientationally disordered molecular solids are a group of solids which retain a high degree of translation correlation in terms of lattice positions of the center of mass but are disordered generally with respect to the position of the substituent groups. Thus, they represent a class inbetween that of an ordered crystalline solid and a truly amorphous medium (it might thus be called an amorphalline solid!) These solids give rise to well defined diffraction patterns that yield a higher average crystal symmetry. The orientational disorder leads to a profound broadening of the spectral profile of the electronic

transitions[6]. The broadening generally results from an inhomogeneous distribution of the site energy (i.e., a variation in the D-shift term in the language of the Frenkel exciton theory)[7].

For understanding the nature of spectral diffusion in a disordered system, these groups of solids are a more useful protosystem than other disordered solids having the following distinct merits:

(i) As the disorder is inherent within the average higher crystal symmetry, it is found to be independent of the history of the crystal preparation. Thus, the observed spectral profile appears to be insensitive to the sample history and is highly reproducible. On the other hand, inhomogeneities in crystals and disorder structure in a glass are very much dependent on the method of the sample preparation creating a problem of reproducibility of spectral profile.

(ii) Often, there is an analog ordered system with which a comparison can be made to discern the effect of disorder both on the electronic states and the phonon bands. The results of investigation of phonon bands indicates that the presence of orientational disorder does not effectively destroy the k-symmetry of the phonon states and thus, no phonon localization is observed. On the other hand, for the case of spectral diffusion for an impurity in a glassy system[4], the possibility of phonon localization at the impurity site becomes a complicating factor in the interpretation of the result.

The present study focuses on a specific system, 1-bromo-4 chloronaphthalene (from here on abbreviated as BCN) which exhibits disorder with respect to the position of the halogens[8]. The observed linewidth[6] of the $T_1 \leftarrow S_0$ absorption of this crystal at 4.2°K is 83 cm^{-1}

(i.e., kT is $\ll$ the linewidth). This linewidth is about two orders of magnitude larger than the linewidth observed ($< 1\ cm^{-1}$) for the corresponding transition in 1, 4 - dichloronaphthalene[6] (DCN) which crystalizes in the same space group with an ordered structure[8], suggesting that the width in BCN is broadened by the orientational disorder. Although the optical phonon transitions observed in the Raman spectra of BCN are found to be broader than that observed for DCN, an excellent phonon spectral correlation[8] between the two crystals reveals that the k-symmetry selection rule for the disordered BCN is not completely destroyed for the optical phonons.

In addition to the fact that BCN is a different type of disordered system than glasses and that the $T_1 \leftarrow S_0$ transition has a linewidth which is much larger than kT, the mechanism of the transfer of the $T_1 \leftarrow S_0$ transition energy is of the exchange type (not dipolar in nature as in the system studied previously[4,5]). The detailed comparision of the nature of the energy diffusion in the two systems would be most important.

EXPERIMENTAL

The BCN was synthesized from 1-amino-4-chloronaphthalene using the procedure described elsewhere[4]. The material was extensively zone refined. Crystals were grown from the melt in a Bridgemann furnace. Samples of 0-5 x 0.5 x 0.2 cm size were mounted in a liquid helium dewar. A Quanta-Ray DCR-1 Nd:YAG pumped pulsed dye laser with a spectral width of $\sim 0.3\ cm^{-1}$ and a pulse width of 6 n sec was used as the $S_0 \rightarrow T_1$ excitation source. The emission was dispersed using a

1 meter Jarrell-Ash monochromator with a 2 cm^{-1} slit width. Time resolved spectra of the first vibronic band of the $T_1 - S_0$ phosphorescence were recorded using a PAR model 162 boxcar averager. A special gated phototube was used in order to reject scattered laser light.

RESULTS

The relationship between the absorption spectra and the emission spectra of the triplet state in 1-bromo-4-chloronaphthalene has been reported elsewhere[6]. It is to be noted that the emission in a steady state experiment is observed from the low energy sites. Furthermore, the width of the emission is about 20 cm^{-1} which is much narrower than the absorption linewidth but is still considerably broader than that observed for the ordered 1,4 dichloronaphthalene triplet emission.

Figure 1 demonstrates that spectral diffusion of the $T_1 \rightarrow S_0$ transition energy occurs in this orientationally disordered material. The band shape of the first vibronic band was monitored as a function of delay time. The spectra displayed were obtained by exciting a site on the low energy side of the $S_0 \rightarrow T_1$ absorption profile. The figure shows that as the delay time increases the resonant type emission decreases in intensity while emission from lower energy acceptors increases in intensity. This figure also shows the same spectra recorded at two different sample temperatures. The phosphorescence spectra obtained under identical conditions but at two different sample temperatures, clearly indicate that the transfer rate is temperature dependent, and thus, phonon assisted[9].

The results of the effect of site selective excitation on the rate of spectral diffusion of the $T_1 \rightarrow S_0$ energy is shown in fig. 2. In each case the spectrum is sampled after a 10 μsec delay using a 50 μsec sampling time. In order to minimize interference with stray light due to the laser,

the first vibronic band profile of the emission is monitored. It can be seen that the observed emission profile is very much dependent on the excitation energy. As the low energy sites are excited, a relatively narrow resonant emission is observed, indicating a transfer rate slower than the sampling time. On the other hand with excitation of higher energy sites, the emission profile is broadened indicating a faster transfer time to a broader distribution of the low energy sites. These observations are suggestive of a transfer rate which at 4.2 K is dependent on the donor site energy.

DISCUSSION

The observed emission line narrowing with the excitation of the low energy sites clearly indicates that the singlet-triplet absorption in BCN is inhomogeneously broadened. The efficient energy transfer from the highest energy sites to the lowest energy sites, without the observation of mobility edges, might suggest the absence of Anderson type localization in this disordered system.

In our previous studies[4] on the transfer of Eu^{3+} excitation in phosphate glasses at room temperature, we found that the full inhomogeneous profile was recovered uniformly with time following pulsed laser excitation, independent of the laser wavelength used. This suggests that the transfer rate is independent of donor-acceptor energy mismatch. This is expected to be the case when kT >> the inhomogeneous width. In our present system, however, kT is $\sim 3\ cm^{-1}$ and the inhomogeneous width is $\sim 80\ cm^{-1}$. Transfer is thus only possible from high to low energy sites at this temperature. This is because transfer from a low energy site to a high energy site requires the population of phonons which is very small at $4.2^{o}K$. For the same reason,

the Raman and Orbach type phonon assisted processes[9] would also be unimportant at this low temperature, thus leaving the direct one phonon emission process as the most probable mechanism for the observed spectral diffusion in this system. For this process, the transfer rate from a donor at site energy E_i can be written as:

$$W_{(E_i)} \propto \Sigma_f \, c_{if,\omega_{if}} \; \rho_{f(E_i)} \; \rho(\omega_{if})(n_{\omega_{if}} + 1) \qquad (1)$$

In this equation c_{if} contains the details of the coupling with phonons required to make up the energy mismatch between the energy of the donor and that of the acceptor; $\rho_{f(E_i)}$ is the density of the acceptor states at energy $\leq E_i$ to which energy can be transferred at 4.2°K by the emission of one phonon. (the inhomogeneous profile can be assumed to result from a distribution of sites). The term n_{if} represents the occupation number of phonons of frequency $\omega_{if} = \frac{E_i - E_f}{\hbar}$ and $\rho(\omega_{if})$ is the phonon density of states. At 4.2°K, $(n_{\omega_{if}} + 1)$ is near unity.

Both for small and large energy mismatch, $c_{if,\omega_{if}} \times \rho(\omega_{if})$ increases with the increase of the energy mismatch (i.e., increase in donor site energy). Furthermore, as the energy of the donor, E_i, increases, the density of the acceptors increases (which leads to an increase in the phase space for the energy transfer process). Thus as a result of all these terms, an increase in the transfer rate is expected as the donor energy increases. This fact explains the lack of emission from sites except the ones at the lowest energy. It also explains our spectral diffusion results which show an increase of the emission from the low energy sites with time upon exiting the higher energy donors.

The observations of the present work are summarized as follows: (i) The spectral profile for the singlet-triplet transition is inhomogeneously broadened by the orientational disorder, (ii) No Anderson type localization is observed for the triplet excitation in this disordered system (iii) The energy transfer is phonon assisted (iv) The spectral diffusion rate is site dependent and increases with an increase in the donor energy.

A more quantitative correlation of the theory and the results will require quantitative measurements of the transfer rates of various low energy sites. Such measurements are in progress and will be reported at a later date.

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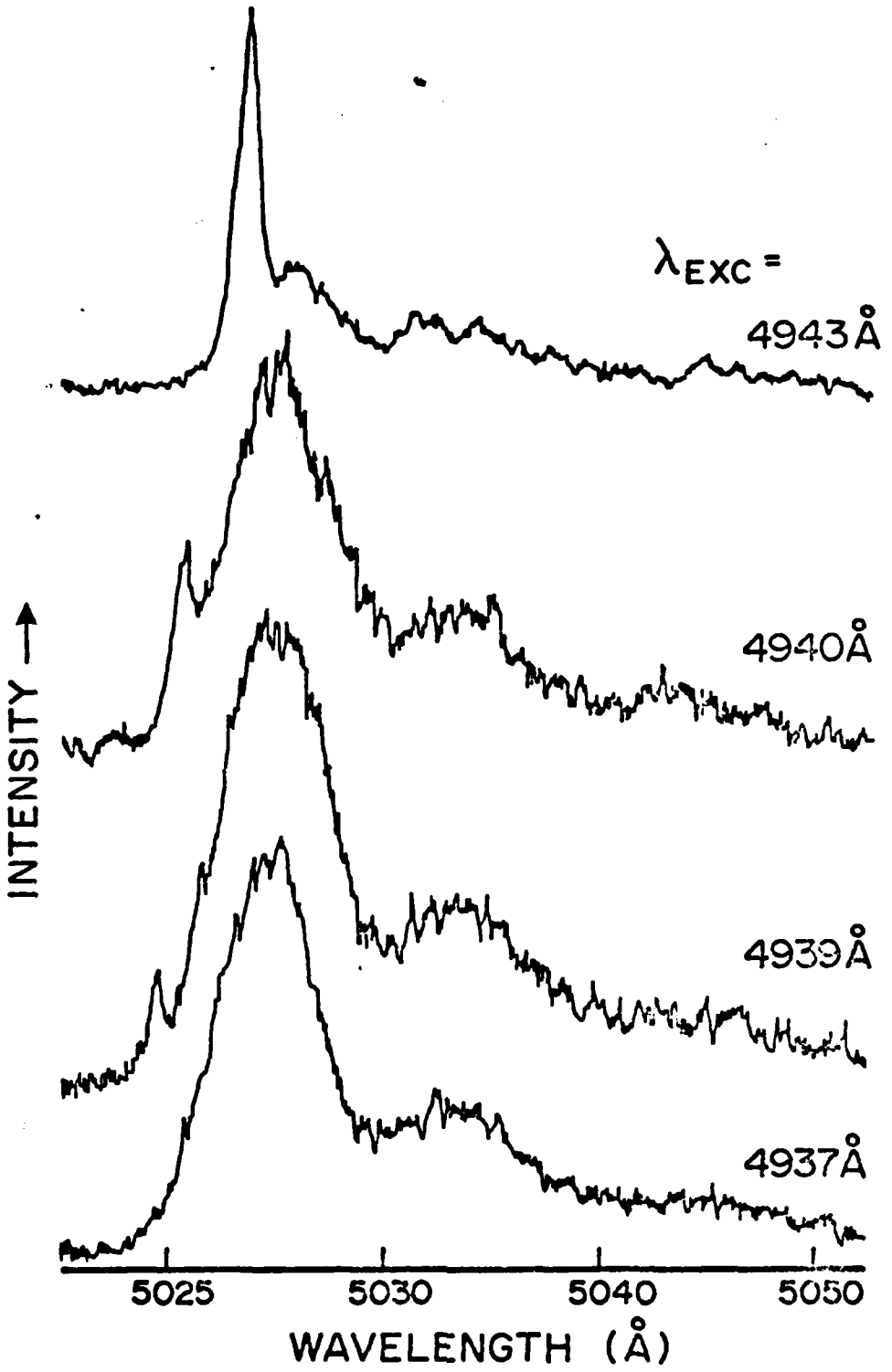
Fig. 1. Spectral diffusion of singlet-triplet excitation energy in an "amorphalline" solid at 4.2°K using time resolved phosphorescence line narrowing techniques. The system is 1-bromO-4-chloronaphthalene excited at 4943 Å. The top three spectra are of the o,o - 321 cm^{-1} vibronic band of the phosphorescence emission recorded at different delay times after the laser pulsed excitation with a 50 μsec sampling time. The bottom spectrum illustrates the effect of temperature on the rate of spectral diffusion within the inhomogeneous profile of the o,o - 321 cm^{-1} band.

Fig. 2. Dependence of the spectral diffusion rate of the singlet-triplet excitation on the donor site energy in 1-bromo-4-chloronaphthalene at 4.2°K. The spectral intensity change of the o,o - 321 cm^{-1} band of the $T_1 \rightarrow S_0$ phosphorescence is monitored with a 10 μsec delay using a 50 μsec sampling time following pulsed laser excitation at different wavelength (i.e., different donor energies) within the inhomogeneously broadened o,o band of the $T_1 \leftarrow S_0$ absorption. The results show that the ratio of the line narrowed (donor) phosphorescence to the lower energy broad emitting traps decreases as the donor (excitation) energy increases, suggesting an increase in the spectral diffusion rate.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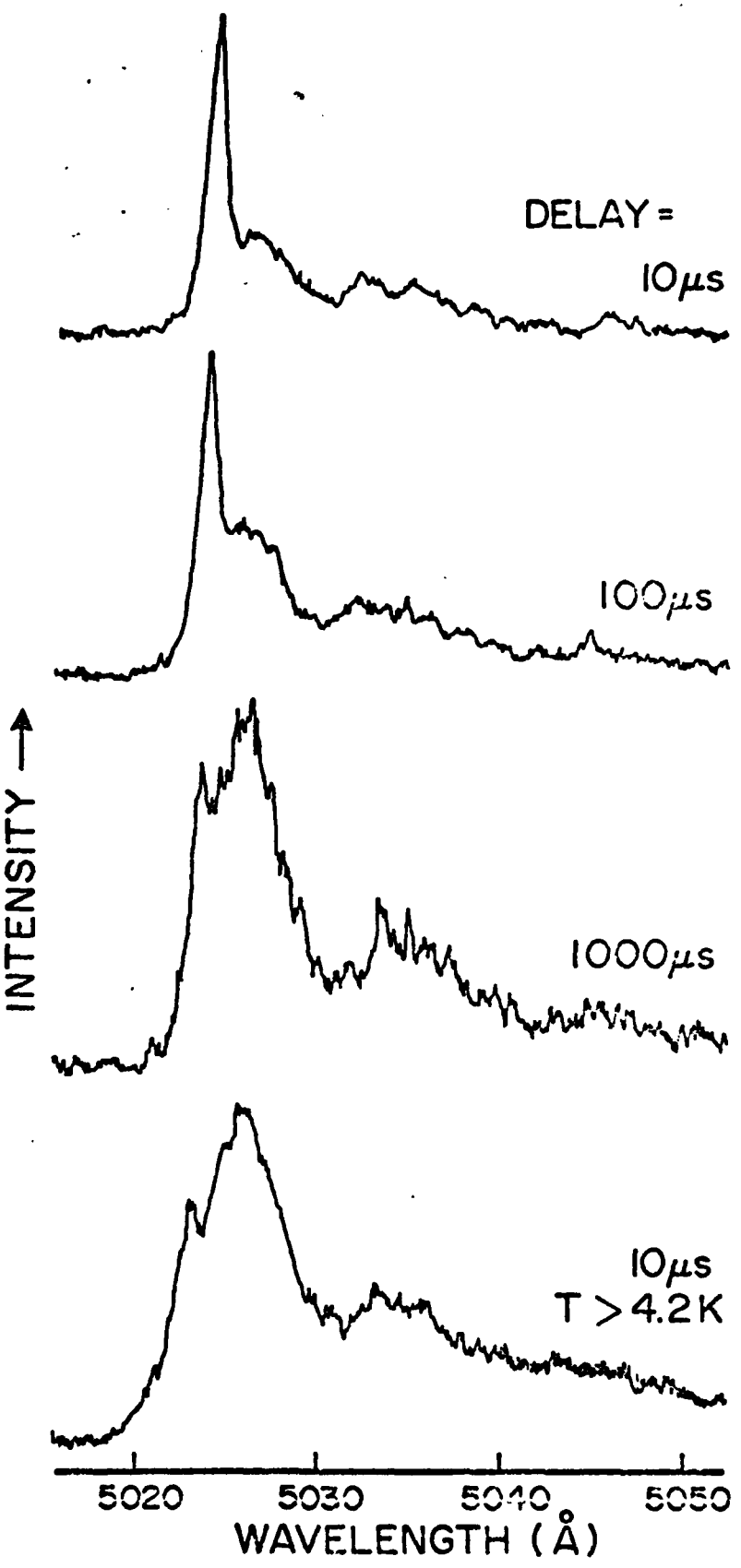
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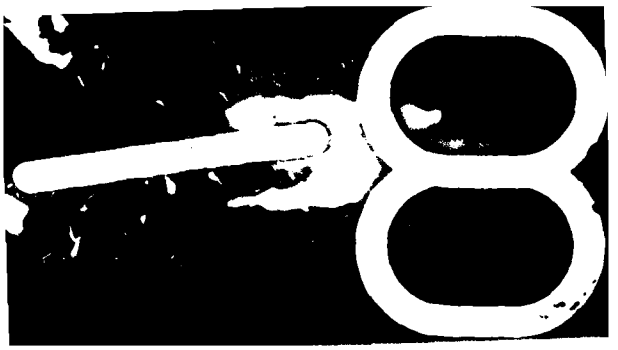
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